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ORIGINAL ARTICLE

Intense quenching of fluorescence intensity of poly(vinyl pyrrolidone) molecules in presence of gold nanoparticles

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Abstract We study the quenching of fluorescence intensity of 40 g/L poly(vinyl pyrrolidone) PVP molecules by varying the content of gold nanoparticles (GNPs) from 1 to 5 μM in 1-butanol. A profound exponential decay of the emission band intensity in the $\pi \leftarrow n\pi^*$ band of the PVP molecules at ~392 nm upon gradual addition of the GNPs demonstrates an existence of an excited state interaction of NPs with the PVP molecules in a gold colloid in 1-butanol. Such quenching is caused by the non-bonding electron transfer from the O-atom of carbonyl group of the PVP molecules to the surface of the GNP. X-ray photoemission spectroscopy (XPS) study corroborates the spectroscopic results. A linear Stern–Volmer plot with a quenching constant of 2.23×10^6 M^{-1} reveals dynamic quenching in a non-aqueous NF. A mechanism of fluorescence quenching was proposed in support of XPS and images taken from hybrid nanostructure using transmission electron microscope. Study on quenching of fluorescence intensity of PVP fluorophore in the presence of GNPs is useful for optoelectronic devices and biosensors.

Keywords Nanoparticle · Fluorescence quenching · Stern–Volmer plot · Electron transfer

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Introduction

Hybrid nanostructures consisting of metal nanoparticles, organic dyes, fluorophores, and oligonucleotides are of recent attraction for various applications such as bioassays (You et al. 2007; Mayilo et al. 2009; Pramanik et al. 2008), biosensors (You et al. 2007), biophotonics (Pramanik et al. 2008; Dulkeith et al. 2002), and biomedicals (Kuo et al. 2012; Zhang et al. 2012). However, gold nanoparticles (GNPs) based composite structures have been receiving considerable attention owing to their stability, biocompatibility, dimensional similarities with biomolecules, and non-toxicity (Pramanik et al. 2008; Kuo et al. 2012; Alexandridis 2011). As the fluorescence quenching technique is an effective method for the study of mechanism of molecular interactions such as excited state interaction and ground-state complex formation, energy and charge transfer, it has been widely used to gather information about biochemical systems (Lakowicz 1999). GNP is found to be an efficient quencher for varieties of light emitting substances (e.g., fluorescent polymers, pyrenes, and organic dyes, etc.), due to its nanometric size and large absorption cross section (Mayilo et al. 2009; Gersten 2005; Ghosh et al. 2004; Dulkeith et al. 2005). GNPs with size ranges from 3 to 22 nm quench the fluorescence intensity of protein Cardiac Troponin T with efficiencies as high as 95 % as compared to bigger particles (Mayilo et al. 2009). Dulkeith et al. (2002) studied the fluroscence quenching of lissamine dye molecules attached to differently sized GNPs using time-resolved fluorescence experiments. A profound quenching by 1 nm GNP was ascribed not only by an increased nonradiative rate but also due to a drastic decrease in the dye's radiative rate. An experimental verification of the size effect of GNPs on quenching of 1-methylaminopyrene (MAP) was done by Ghosh et al.

(2004). As suggested by the authors, the large surface to bulk atom ratio of GNPs is responsible for the efficient quenching of emission intensity of MAP molecules.

In this article, we studied the decrease in the fluorescence intensity of poly(vinyl pyrrolidone) PVP molecules by varying the GNPs content in 1-butanol. The formation of GNPs in a non-hydrocolloid was confirmed by UV–visible, X-ray photoemission spectroscopy (XPS), and transmission electron microscope (TEM). An organic solvent was chosen in this work because such medium founds to provide low interfacial energies needed for a high degree of control during solution and surface processing is required for synthesis of nano colloids (Balasubramaniam et al. 2002). Also it was reported that Au-NPs synthesized in an organic medium offer excellent control over size and possess superior processability (Sugunan et al. 2005).

Materials and methods

Chemicals and instruments

We used reagent grade $Au(OH)_3$ powder purchased from Alfa Aesar. It was dissolved in dilute nitric acid to prepare a stock solution of 0.05 M $Au(NO_3)_3$. PVP (25 kDa) and 1-butanol were purchased from Sigma Aldrich and Merck, respectively. The chemicals were used as received, without further purification.

The UV–visible spectrum of Au non-hydrocolloid with PVP molecules was measured on a Perkin Elmer double beam spectrophotometer (LAMBDA 1050). The sample was filled in a transparent cell of quartz (10 mm path length), and the spectrum was recorded against a reference of 1-butanol with 40 g/L PVP in an identical cell. X-ray photoelectron spectrum (XPS) was collected on a VG ESCALAB MK-II spectrometer with a monochromatic Al Kα source ($h\nu = 1{,}486.6$ eV) operated at 10 kV and 20 mA at 10^{-9} Pa. The sample for XPS was prepared by drop-casting a small aliquot of Au colloid with PVP in 1-butanol on silicon substrate and dried in desiccators by keeping overnight at room temperature. The photoluminescence spectra have been recorded with a computer controlled Perkin–Elmer (Model-LS 55) luminescence spectrometer in conjugation with a red sensitive photo multiplier tube detector (RS928) and a high energy pulsed xenon discharge lamp as an excitation source (average power 7.3 W at 50 Hz). A quartz cell of 10 mm width was used as sample holder.

Microscopic images of PVP-encapsulated GNPs were studied with a high-resolution transmission electron microscope (HRTEM) of JEM-2100 (JEOL, Japan) operated at an accelerating voltage of 100 kV. The samples were prepared by dropping one drop of diluted solution on a carbon coated 400 mesh copper grid, and then allowing the samples to dry in desiccators overnight at room temperature.

Preparation of PVP-capped GNPs

At first, we prepared an organic mother solution of PVP (40 g/L) in 1-butanol by mechanical stirring for 3 h at 60–70 °C. After cooling the PVP solution to room temperature, a specific volume of gold nitrate solution was added drop wise while stirring to four different batches, each of 5 mL of 40 g/L PVP solution in 1-butanol at 50 °C. After continuously hot magnetic stirring for 20 min, we obtained series of purple colored Au colloids (with intensity increases with GNPs content) consisting of 1, 2, 3, and 5 μM GNPs with 40 g/L PVP molecules, in 1-butanol.

Results and discussion

UV–visible and XPS spectrum

As shown in the Fig. 1a, UV–visible absorption spectrum for Au colloid consisting of 1 μM GNPs in the presence of 40 g/L PVP molecules in 1-butanol displayed a strong peak at 526 nm ascribed to surface plasmon resonance (SPR) band (Eustis and El-Sayed 2006; Sugunan et al. 2005; Ram and Fecht 2011; Behera and Ram 2012a, b). Whereas absorption spectrum of 1 μM uncapped-GNPs (i.e., without PVP molecules) in 1-butanol exhibits a somewhat red-shifted and broad SPR band at 533 nm with a half width at full maximum (HWFM) ~65 nm shown in the inset of Fig. 1a. In the presence of PVP molecules, this band blue shifted to 526 nm as a result of quantum confinement effect (Eustis and El-Sayed 2006; Behera and Ram 2012a, b). Again the SPR band with a comparatively small value of HWFM ~48 nm implies that PVP acts as a good stabilizing agent and reduces the polydispersity in GNPs in the non-aqueous colloid (Alexandridis 2011; Behera and Ram 2012a, b). We studied the XPS spectrum obtained from PVP-capped GNPs to confirm the formation of NPs. Figure 1b depicts the XPS spectrum recorded of 4f photoelectrons of 1 μM GNP with PVP. The deconvolution of Au4f doublet bandgroup shows one band at binding energy of 85.98 eV and other one at 82.25 eV assigned of $Au4f_{5/2}$ and $Au4f_{7/2}$ peak, respectively. A chemical shift of 3.73 eV confirms reduction of Au^{3+} to Au^0 valance state in the reaction medium (Ram and Fecht 2011; Joseph et al. 2003; Patnaik and Li 1998; Abyaneh et al. 2007). A negative shift in binding energy of both $4f_{7/2}$ and $4f_{5/2}$ band in GNP with PVP molecules as compared to bulk Au atom reveals an interaction between GNP and PVP polymer molecules (Joseph et al. 2003; Patnaik and Li 1998; Abyaneh et al. 2007).

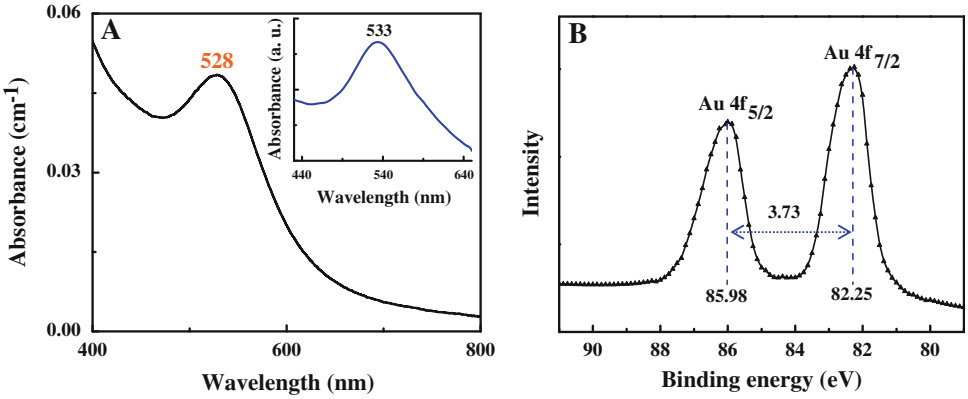

Fig. 1 **a** UV–visible absorption and **b** XPS spectrum of Au colloid consisting of 1 μM GNPs with 40 g/L PVP in 1-butanol. Absorption spectrum of 1 μM Au colloid without PVP in 1-butanol is shown as in *inset* (**a**)

Microstructural analysis

Figure 2 depicts microscopic images obtained from 1 μM GNP with PVP molecules. The GNPs are encapsulated in PVP molecules in such a way that they appear mostly of spherical shapes of 5–10 nm diameters. As seen from the image (Fig. 2a), PVP-encapsulated GNPs demonstrate a distinct amorphous surface layer (shell) of PVP (as a whitish contrast) which coats firmly to the darkish region of the GNP (core). As an electron beam can easily pass through an amorphous layer, it appears of whitish contrast in such hybrid nanostructure. Such type of feature has already been reported in PVP-encapsulated GNPs (Ram and Fecht 2011; Behera and Ram 2012a, b). Rahme et al. (2008) have also reported a similar kind of core–shell nanostructures in a block copolymer-capped GNPs. The crystalline nature of Au-core was identified by diffraction rings (Fig. 2b) obtained from bulk of GNP. A high-resolution TEM image (Fig. 2c) obtained from PVP-encapsulated GNP displaying lattice fringes confirms crystalline structure of GNP with inter planar spacing of 0.233 nm corresponding to (111) plane of face centered cubic Au lattice (Ram and Fecht 2011; Behera and Ram 2012a, b).

Photoluminescence (PL) spectra

Emission and excitation spectra

The emission spectra (320–560 nm) of (a) 40 g/L PVP solution and Au colloids consisting of (b) 1.0, (c) 2.0, (d) 3.0, and (e) 5.0 μM GNPS with 40 g/L PVP in 1-butanol, excited at 300 nm are shown in Fig. 3a. The emission band at 392 nm is ascribed to $\pi \leftarrow n\pi^*$ band transition in PVP molecules (Ram and Fecht 2011). The normalized emission intensity (I_{Em}) of PVP molecules is found to be quenched by addition of GNPs (Fig. 3b). The addition of GNPs (1 μM) caused 74 % quenching of polymer emission intensity and reached about 93 % after adding 5 μM GNPs. Such an exponential decay of emission intensity is ascribed to the existence of a donor–acceptor type interaction between GNP and PVP molecules, as non-bonding (n) electron transfer occur from O-atom of C=O group of PVP molecules to the GNP (Pramanik et al. 2008; Dulkeith et al. 2002; Ghosh et al. 2004; Karthikeyan 2010). A redshift in the 392 nm band in PVP molecules in the presence of GNPs signifies an energy loss due to electron transfer from C=O groups to the

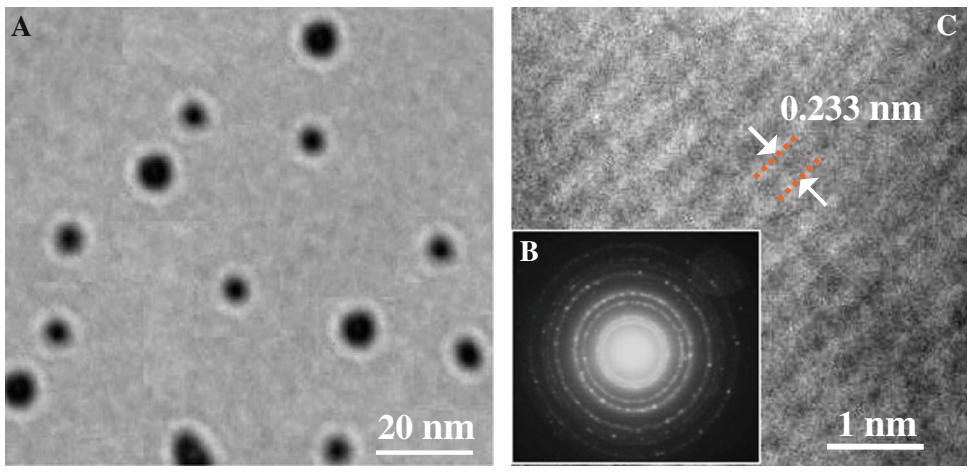

Fig. 2 **a** TEM images taken from 1 μM GNPs with 40 g/L PVP molecules. Rings of electron diffraction pattern (**b**) and lattice fringes (**c**) reveals crystalline nature of PVP-encapsulated GNPs

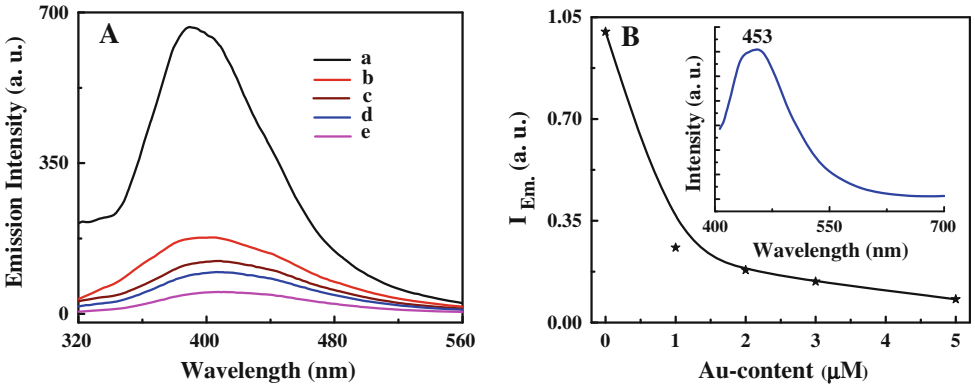

Fig. 3 **a** Emission spectra of 40 g/L PVP with different Au-content in 1-butanol; *a* 0, *b* 1.0, *c* 2.0, *d* 3.0, and *e* 5.0 μM, excited at 300 nm. **b** Shows variation of normalized emission intensity with Au-content. An emission spectrum of 1 μM Au colloid without PVP in 1-butanol excited at 240 nm is shown as in *inset* (**b**)

electron deficient GNP. As shown in the inset of Fig. 3b, a band at 453 nm in the emission spectrum of 1 μM GNPS without PVP molecules excited at 240 nm is assigned to inter-band transition from sp-conduction band above the Fermi level to the d-band below in GNP (Eustis and El-Sayed 2006; Mooradian 1969; Varnavski et al. 2001).

Figure 4a shows the excitation spectra (300–380 nm) of (a) 40 g/L PVP solution and Au colloids consisting of (b) 1.0, (c) 2.0, (d) 3.0, and (e) 5.0 μM GNPS with 40 g/L PVP in 1-butanol, with emission wavelength 400 nm. As shown in Fig. 3b, an exponential decrease in the normalized excitation intensity (I_{Exc}) of PVP molecules in the presence of GNPs is attributed to existence of a donor–acceptor type interaction between GNP and PVP molecules, as a result of *n*-electron transfer from O-atom of C=O group of PVP molecules to the GNP (Dulkeith et al. 2002; Ghosh et al. 2004; Karthikeyan 2010). An excitation spectrum of 1 μM GNP without PVP molecules in 1-butanol emitted at 380 nm exhibit a band at 276 nm is due to d-band to conduction band transition in GNP (Eustis and El-Sayed 2006; Mooradian 1969; Varnavski et al. 2001).

Stern–Volmer plot

The PL quenching technique is an effective method for the study of the mechanism of the molecular interaction, energy transfer, or charge transfer. The Stern–Volmer equation (Lakowicz 1999) accounting for PL quenching is written as:

$$F_0/F = 1 + K_{SV}[Q], \quad (1)$$

where F_0 and F are the emission intensities of PVP molecules in the absence and presence of quencher (i.e., GNPs); $[Q]$ is the concentration of quencher (i.e., GNP) and K_{SV} is quenching constant which tells about efficiency of quenching.

Figure 5 demonstrates the dependence of F_0/F on the concentration of GNP. The linearity of plot indicates that only one type of quenching occurs in the system (Pramanik et al. 2008; Lakowicz 1999). The K_{SV} value can be obtained from the slope of the linear plot and found to be 2.23×10^6 M^{-1}. Such a large value suggests existence of strong interaction between PVP molecules and GNP via O-atom of carbonyl group (You et al. 2007; Alexandridis 2011; Ghosh et al. 2004), and reveals dynamic quenching mechanism in our system (Ghosh et al. 2004). In support of XPS spectrum, TEM images, and PL spectra, we proposed a quenching mechanism which has been represented in Fig. 6. An electron rich PVP molecule gets adsorbed readily onto a metal surface via *n*-electrons of C=O groups (Fig. 6a), and forms a core–shell hybrid structure (Fig. 6b) with Au crystalline core covered by an amorphous PVP-surface layer. A similar adsorption mechanism facilitated

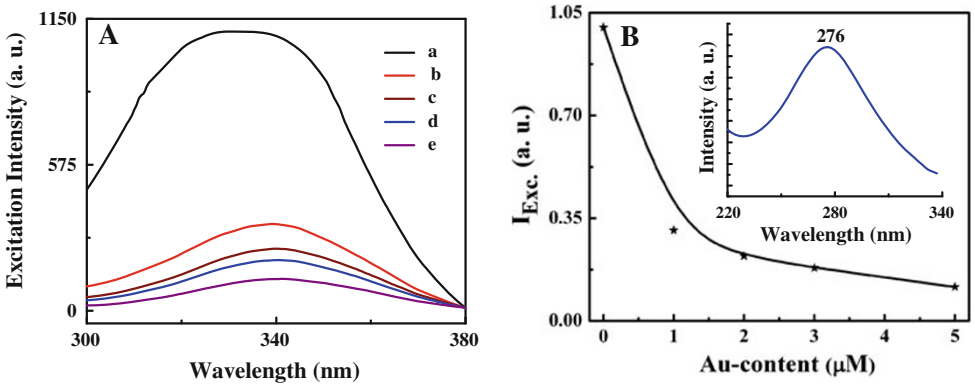

Fig. 4 **a** Excitation spectra of 40 g/L PVP with different Au content in 1-butanol; *a* 0, *b* 1.0, *c* 2.0, *d* 3.0, and *e* 5.0 μM, emitted at 400 nm. **b** Shows variation of normalized excitation intensity with Au-content. An excitation spectrum of 1 μM Au colloid without PVP in 1-butanol emitted at 380 nm is shown as in *inset* (**b**)

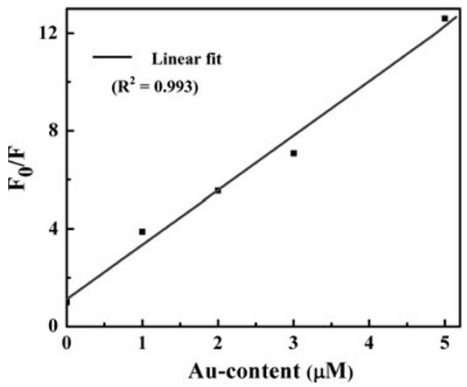

Fig. 5 Stern–Volmer plot of F_0/F versus Au-content. The linear fit gives $F_0/F = 1.11 + 2.23$ [Au]

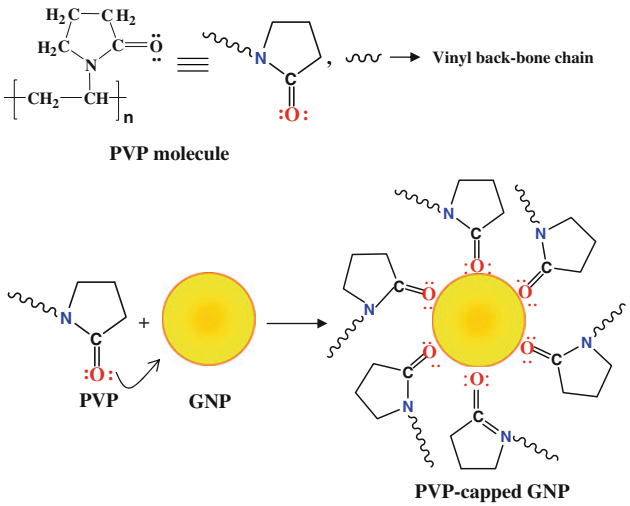

Fig. 6 Schematic presentation of adsorption PVP molecules onto the active surface of GNP via *n*-electron transfer from O-atom of C=O group to GNP

by *n*-electron of MAP had already been proposed for MAP-capped GNP (Ghosh et al. 2004). Pramanik et al. (2008) have proposed a likewise adsorption mechanism to support the PL quenching of bovine serum albumin molecules in the presence of GNPs.

Conclusions

GNPs efficiently quench the PL intensity of PVP molecules in 1-butanol. An exponential decay of PL intensity in the $\pi \leftarrow n\pi^*$ band of PVP molecules at $\sim$392 nm in the presence of GNPs suggest an excited state interaction between GNP and PVP molecules. A large $K_{SV} = 2.23 \times 10^6\ M^{-1}$ reveals a dynamic quenching mechanism. Profound PL quenching of biopolymer in the presence of biocompatible quencher such as GNP is suitable for biosensors, bioassays, biomedical, and biophotonics applications.

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